



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 630 044 A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 94114930.4

(51) Int. Cl.⁵: H01L 21/90

(22) Date of filing: 15.08.89

This application was filed on 22 - 09 - 1994 as a divisional application to the application mentioned under INID code 60.

(30) Priority: 08.09.88 JP 223503/88

(43) Date of publication of application:
21.12.94 Bulletin 94/51

(60) Publication number of the earlier application in accordance with Art.76 EPC: 0 358 350

(64) Designated Contracting States:
DE FR GB

(71) Applicant: KABUSHIKI KAISHA TOSHIBA
72, Horikawa-Cho
Saiwai-ku
Kawasaki-shi
Kanagawa-ken (JP)

(72) Inventor: Okumura, Katsuya, c/o Intellectual Property Div.

Toshiba Corporation,
1-1-1, Shibaura
Minato-ku,
Tokyo (JP)
Inventor: Watanabe, Tohru, c/o Intellectual Property Div.
Toshiba Corporation,
1-1-1, Shibaura
Minato-ku,
Tokyo (JP)
Inventor: Watase, Masami, c/o Intellectual Property Div.
Toshiba Corporation,
1-1-1, Shibaura
Minato-ku,
Tokyo (JP)

(74) Representative: Maury, Richard Philip et al
MARKS & CLERK,
57-60 Lincoln's Inn Fields
London WC2A 3LS (GB)

(54) Forming a prescribed pattern on a semiconductor device layer.

(57) A method for forming a prescribed pattern on a layer of a semiconductor device, comprising the steps of:

preparing a substrate (40) having a first main surface;

forming a first layer (41) on the first main surface;

forming a second layer (42) on the first layer;

forming a third layer (43) on the second layer;

selectively removing the third layer to form a first patterned layer;

immersing the substrate having the first patterned layer into a predetermined solution to form a fourth layer (45) selectively over the portions of the second layer uncovered by the first patterned layer;

removing the first patterned layer; and

etching the second layer using the fourth layer (45) as a mask,

characterised in that the first layer (41) is an insulating layer, the second layer (42) is a metal layer, third layer (43) is a photoresist layer, and the fourth layer is a SiO₂ layer, whereby the remainder of the second layer (42) constitutes a metal interconnect layer for the semiconductor device.

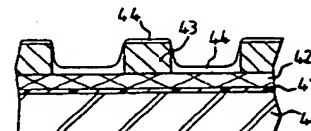


FIG. 4A

EP 0 630 044 A2

BEST AVAILABLE COPY

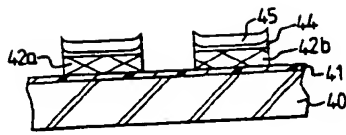


FIG. 4D

This invention concerns a method for forming a prescribed pattern of, e.g., a wiring layer by etching, on a semiconductor device.

Conventionally, for etching a semiconductor substrate, a Reactive Ion Etching (RIE) is utilized using a photoresist pattern formed on the semiconductor substrate as a mask.

FIG.1 is a diagram for explaining a problem which is present in a conventional process for forming a pattern of submicron dimensions using a conventional exposure and development technique. Namely, in the case where the width between the adjacent pattern is relatively wide, e.g. 1.0 μm , a desired pattern may be obtained by the conventional technique. However, in the case where the width is 0.8 μm (e.g., between the photoresist pattern 12 and 13), some undeveloped photoresist remains on the substrate 10, since the bottom portion of the photoresist is not sufficiently exposed even if the upper portion is clearly patterned. Thus, it is difficult to use the photoresist pattern 12 and 13 as a mask in a subsequent etching process.

FIGS.2A and **2B** are diagrams for explaining a problem in a conventional process for forming a prescribed pattern of a high reflective metal layer 21 in a recessed portion 24 of a semiconductor substrate 20. In the conventional process, a material of high reflectivity, such as a tungsten silicide 21, is formed. A photoresist layer 23 is then formed thereon (Fig. 2A). Next, an exposure and a development are carried out to form a photoresist pattern 23a and 23b. By this process, a desired pattern 23a and 23b of photoresist may be formed on a flat surface of the substrate 20. However, at the level difference portion 24, the reflected light from the angled surface 22 of the metal layer 21 exposes the photoresist 23 in the recess. Thus, the desired pattern illustrated by the dotted line 23c cannot be obtained, and a photoresist pattern 23d may result instead. Therefore, it is also difficult to use the pattern 23d as a mask to etch the metal layer 21 accurately.

It is known from U.S. Patent No. 4599137 to provide a method, as defined in the pre-characterizing portion of Claim 1, of forming a resist micro-pattern in a semiconductor device manufacturing process. Further, U.S. Patent No. 4624 749 discloses the use of a metal (gold) as an interconnect layer, formed by gold-electroplating selectively over a photoresist pattern which is complementary to the desired gold interconnect pattern.

An object of the present invention is to provide an improved method which results in a desired accurate photoresist pattern, even if the width between the adjacent portions of the pattern is of the submicron order.

To achieve the object, this invention provides a method as defined in Claim 1 and in Claim 2 for

forming a prescribed pattern on a layer of a semiconductor device.

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate embodiments of the invention, and, together with the description, serve to explain the principles of the invention. Referring now to the drawings, like reference characters designate like or corresponding parts throughout the several views. Of the drawings:

FIG. 1 is a cross sectional view for explaining a problem in a conventional process.

FIGS. 2A and **2B** are drawings for explaining another conventional process and the problem inherent therein.

FIGS. 3A to **3D** are cross sectional views for explaining an embodiment of the present invention.

FIGS. 4A to **4D**, **FIGS. 5A** to **5E**, **FIGS. 6A** to **6D** and **FIGS 7A** to **7D** are cross sectional views of structures not made using the present invention but included for background information.

Referring now to the drawings, the present invention will be explained in detail.

FIGS. 3A to **3D** are cross sectional views for explaining an embodiment of the present invention, which allows formation of a wiring pattern at a recessed portion of a semiconductor substrate.

At first, a semiconductor substrate 30 having a recessed portion or a dent 34 is prepared. Then, a tungsten silicide layer 31 to be patterned is formed on the substrate 31. Next, a positive photoresist layer, e.g., an OFPR (manufactured by Tokyo Oka Co.), is formed over the entire surface, and a photoresist pattern 33a and 33b covering a wall 32 at the dent 34 is formed using a conventional exposure and development technique. (**FIG.3A**)

Next, the substrate 30 is immersed into a silicofluoride aqueous solution. In this step, a silicon oxide (SiO_2) layer 35 of about 1000 Å is selectively formed at the area where the tungsten silicide (WSi) layer 31 is exposed, since the H_2SiF_6 and H_2O react to precipitate SiO_2 . To selectively form the SiO_2 layer, the surface of the photoresist layer 33a and 33b are subjected to, e.g., an oxygen plasma, to change the surface thereof from a hydrophilic condition (having, e.g., -OH radical as an end radical) to a hydrophobic condition (having, e.g., -O radical as an end radical), preferably. (**FIG.3B**) This process is referred to as a hydrophobic treatment hereafter.

Then, the photoresist pattern 33a and 33b are removed by, e.g., an ashing. (**FIG.3C**)

Next, an anisotropic etching, such as a RIE, is carried out to form a desired WSi wiring layer 31a, 31b and 31c using the SiO_2 layer 35 as a mask. (**FIG.3D**) Then, an etching for removing the SiO_2 layer 35 follows thereafter. (not shown)

According to this process, the wall 32 at the

dent 34 is not exposed. Thus, the problem due to the light reflection from the surface 32 can be prevented. Furthermore, the etching selectively between the WSi and the SiO₂ is relatively high. Therefore, it is possible to obtain a desired pattern of WSi wiring 31a on the substrate 30, even if the substrate 30 includes a recessed portion, since the SiO₂ layer 35 having a relatively low etching rate is used as a mask to etch the WSi layer 31.

It is, of course, possible to use other materials for the wiring layer, as one of ordinary skill in this art will realise.

The following description is included as background, even though the examples do not embody the invention.

FIGS. 4A to 4D are cross sectional views. On a semiconductor substrate 40, a thermal oxide layer 41 is formed. On the oxide layer 41, an aluminium layer (Al) 42 of about 8000 Å to be etched is formed by, e.g., sputtering. Then, a patterned photoresist pattern 43 of about 12,000 Å is formed on the Al layer 42 using a conventional exposure and development technique. Next, a glass layer 44 is formed by a Spin on Glass (SOG) method following a baking treatment. (FIG. 4A) Then, a conventional etching process is carried out to remove the relatively thin glass layer formed on the photoresist 43, and to leave a portion of the relatively thick glass layer 44 formed where the photoresist layer 43 is not formed. Next, a hydrophobic treatment is carried out.

Then, the substrate is immersed into a silicofluoride aqueous solution to form a SiO₂ pattern 45 of about 2000 Å on the glass layer 44, selectively. (FIG. 4B)

Next, the photoresist pattern 43 is removed by, e.g., a wet etching. (FIG. 4C)

Then, an anisotropic etching, e.g., a RIE, is carried out

to form a desired Al wiring layer 42a and 42b using the SiO₂ pattern 45 as a mask. (FIG. 4D) Then, an etching for removing the SiO₂ layer 45 and the glass layer 44 is carried out (not shown).

In this process, the etching selectivity between the Al layer and the SiO₂ layer is about 10, and is relatively large compared with that of between the Al layer and the photoresist layer, namely about 2. Thus, the selectivity of the etching can be improved. Furthermore, the remaining Al pattern 42a and 42b is determined by the SiO₂ layer 45. The area where the SiO₂ layer is formed is determined by the remaining photoresist layer 43. Thus, the narrower the photoresist pattern 43 becomes, the wider the Al pattern 42a and 42b becomes. It is easy to make the remaining photoresist pattern narrower by controlling the exposing condition, e.g. by an over exposure, since the photoresist is a positive photoresist. This means that the width be-

tween the adjacent patterns can be made narrower, and the resolution can be improved.

In this process, the glass layer 44 serves to protect the Al layer 42 from etching during the immersion of the substrate into the solution for precipitating the SiO₂ layer 42.

FIGS. 5A to 5E are drawings of a further example.

On a semiconductor substrate 50, a thermal oxide layer 51 is formed. On the oxide layer 51, a aluminium layer (Al) 52 of about 8,000 Å to be etched is formed by, e.g., a sputtering. Then, a glass layer 53 is formed by a Spin on Glass method following a baking treatment. Then, a patterned photoresist layer 54a, 54b and 54c is formed using a conventional exposure and development technique. (FIG. 5A)

After a hydrophobic treatment of the photoresist pattern 54, the substrate is immersed into a silicofluoride aqueous solution to form a SiO₂ layer 55. (FIG. 5B)

Then, the resist layer 54 is removed. (FIG. 5C)

Next, an etching, e.g., a wet etching, is carried out to etch the glass layer 53 using the SiO₂ layer 55 as a mask. (FIG. 5D)

Then, an anisotropic etching, e.g., a RIE etching, is carried out to form a desired Al wiring layer 52a and 52b using the SiO₂ layer 55 as a mask. (FIG. 5E) Then, the glass layer 53 and the SiO₂ layer 55 are removed (not shown). Using this process, a desired wiring pattern can be achieved, as in the example illustrated in FIGS. 4A to 4D.

FIGS. 6A to 6D are drawings for explaining a further example of forming a contact hole in a semiconductor device. On a semiconductor substrate 60, an insulating layer 61 is formed. Then, a polysilicon layer 62 of about 300 Å is formed on the insulating layer by, e.g., a low pressure CVD method. Next, a patterned photoresist layer 63 is formed on the polysilicon layer 62 using a conventional exposure and development technique. (FIG. 6A) Then, a hydrophobic treatment of the photoresist layer 63 is carried out.

Next, the substrate is immersed into a solution of palladium chloride (PdCl₂) to form a palladium layer 64 of less than 100 Å using a non-electric plating method. Next, the substrate is immersed into a mixed solution of nickel sulfate (NiSO₄) and hypophosphite to form a nickel layer 65 of about 1000 Å. (FIG. 6B)

Next, the photoresist layer is removed by, e.g., an ashing treatment using an oxygen plasma. (FIG. 6C)

Then, an anisotropic etching, e.g., a RIE, is carried out to form a contact hole 66 using the nickel layer 65 as a mask. (FIG. 6D)

Next, the nickel layer 65 and the palladium layer 64 are removed by a wet etching using a

mixed etchant of a hydrochloric acid, a nitric acid and an acetic acid. The polysilicon layer 62 may either be removed by a wet etching using an organic alkali solution, e.g., a choline or a dry etching using a fluorine as an active radical, or it may be oxidized and left as it is.

In this example, the size of the contact hole 66 is determined by the remaining photoresist pattern 63. Thus, by narrowing the size of the photoresist layer 63 using, e.g., an over exposure, it is possible to form a resist pattern having a narrower width than the resolution limit. Thus, it is possible to form a narrower contact hole than when the conventional etching process is used. Furthermore, the etching rate of the nickel layer 65 is extremely smaller than that of the insulating layer 61. Thus, a desired fine contact hole can be formed easily. The palladium layer 64 provides a good adhesion between the polysilicon layer 62 and the nickel layer 65.

FIGS.7A to 7D are drawings for explaining a further example of oxidizing a semiconductor substrate 70. On a semiconductor substrate 70, a thermal insulating layer 71 is formed. Then, a silicon nitride layer 72 is formed on the insulating layer 71. Next, on the silicon nitride layer 72, a patterned photoresist layer 73 is formed. (FIG.7A)

After a hydrophobic treatment of the photoresist layer 73, the substrate is immersed into the same solution, in the same way, as the embodiment of FIGS.3A to 3D, to form a SiO₂ layer 74.

Next, the photoresist layer 73 is removed by, e.g., ashing using an oxygen plasma. (FIG.7C)

Then, the silicon nitride layer 72 is selectively etched by using the SiO₂ layer 74 as a mask. An oxidizing treatment is then carried out to oxidize the substrate 70 to form a device separating oxide layer 75, using the silicon nitride layer 72 selectively remaining under the SiO₂ layer 74 as a mask layer. (FIG.7D) Next, an etching treatment, e.g., a Chemical Dry Etching (CDE) is carried out to remove the SiO₂ layer 74 and the silicon nitride layer 72.

In the examples of Figures 3, 4, 5 and 7, a SiO₂ layer formed by a precipitation is used as a mask layer. However, it is possible to use a nickel layer formed by a non-electric plating process, as used in Fig. 6, as a mask layer, and vice versa. Thus, in each example, either a SiO₂ layer or a nickel layer may be used as the mask layer.

Furthermore, it is possible to etch the semiconductor substrate instead of the wiring layer and the insulating layer.

Moreover, it is possible to utilize the present invention to form a pattern on an optical disk for storing a information.

In the aforementioned examples, a photoresist layer is used for the pattern formation. However, any film layer can be used as long as the layer

permits little or no precipitation of substances thereon during immersion.

The present invention has been described with respect to a specific embodiment. However, other embodiments should be apparent to those of ordinary skill in the art. Such embodiments are intended to be covered by the claims.

Claims

1. A method for forming a prescribed pattern on a layer of a semiconductor device, comprising the steps of:
 - preparing a substrate (40) having a first main surface;
 - forming a first layer (41) on the first main surface;
 - forming a second layer (42) on the first layer;
 - forming a third layer (43) on the second layer;
 - selectively removing the third layer to form a first patterned layer;
 - immersing the substrate having the first patterned layer into a predetermined solution to form a fourth layer (45) selectively over the portions of the second layer uncovered by the first patterned layer;
 - removing the first patterned layer; and
 - etching the second layer using the fourth layer (45) as a mask,
 characterised in that the first layer (41) is an insulating layer, the second layer (42) is a metal layer, third layer (43) is a photoresist layer, and the fourth layer is a SiO₂ layer, whereby the remainder of the second layer (42) constitutes a metal interconnect layer for the semiconductor device.
2. A method for forming a prescribed pattern on a layer of a semiconductor device, comprising the steps of:
 - preparing a substrate (40) having a first main surface;
 - forming a first layer (41) on the first main surface;
 - forming a second layer (42) on the first layer;
 - forming a third layer (43) on the second layer;
 - selectively removing the third layer to form a first patterned layer, immersing the substrate having the first patterned layer into a predetermined solution to form a fourth layer (45) selectively over the portions of the second layer uncovered by the first patterned layer;
 - removing the first patterned layer; and
 - etching the second layer using the fourth

layer (45) as a mask;

characterised in that the first layer (41) is an insulating layer, the second layer (42) is a metal layer, third layer (43) is a photoresist layer, and the fourth layer is a metal layer, whereby the remainder of the second layer (42) constitutes a metal interconnect layer for the semiconductor device.

3. A method according to claim 1, further comprising the step of forming a glass layer (44) on the second layer (42) before the formation of the fourth layer (45). 5
4. A method according to claim 3, wherein the glass layer (44) is formed by a Spin on Glass method. 10
5. A method according to claim 1, further comprising the step of forming a sixth layer (53) as the upper layer of the second layer (52) before the formation of the third layer (54), so that the sixth layer is etched using the fourth layer (55) as a mask. 15
6. A method according to claim 2, wherein the fourth layer (65) is a nickel layer. 20

25

30

35

40

45

50

55

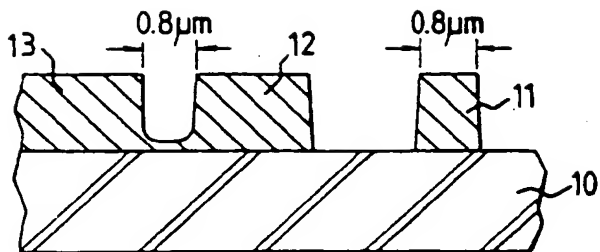


FIG. 1
PRIOR ART

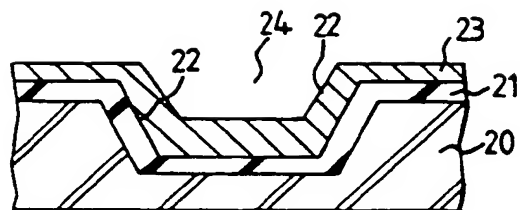


FIG. 2A

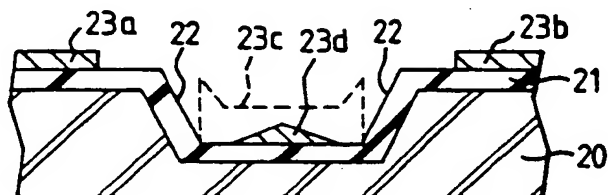


FIG. 2B
PRIOR ART

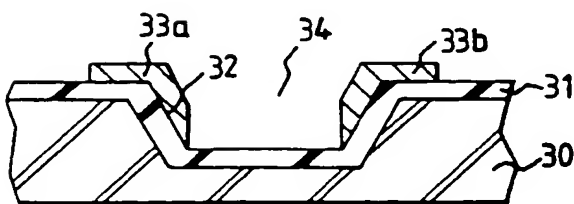


FIG. 3A

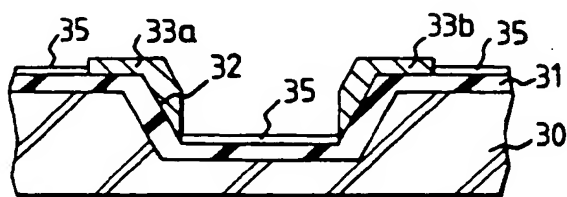


FIG. 3B

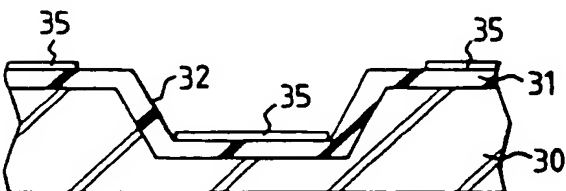


FIG. 3C

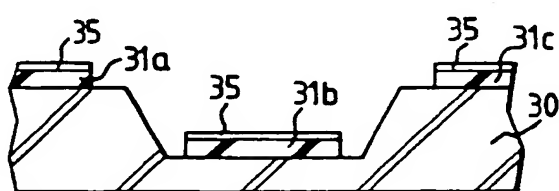


FIG. 3D

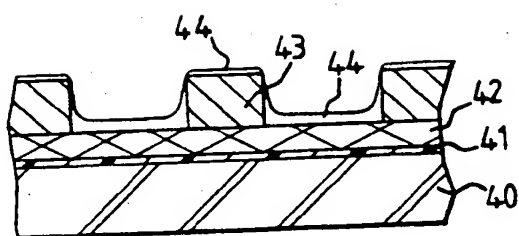


FIG. 4A

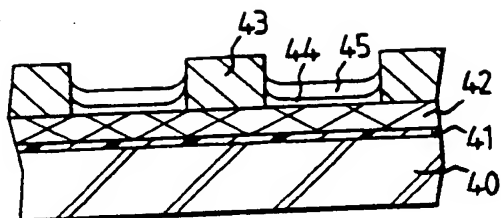


FIG. 4B

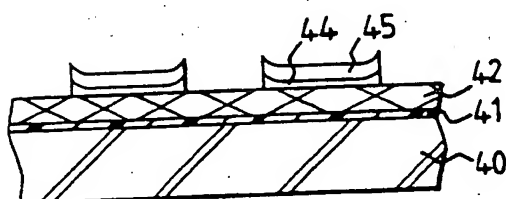


FIG. 4C

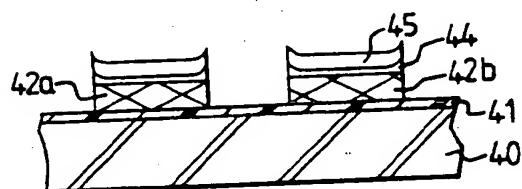


FIG. 4D

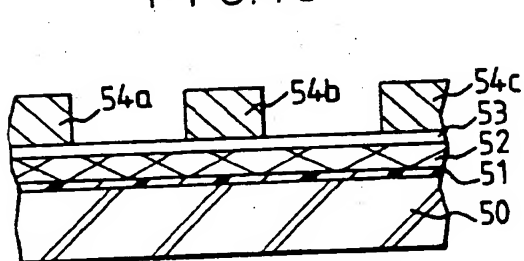


FIG. 5A

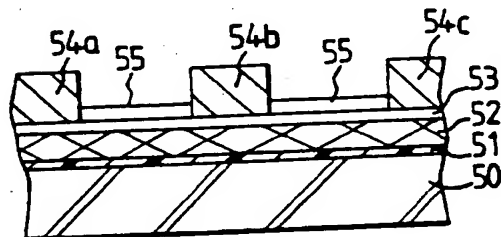


FIG. 5B

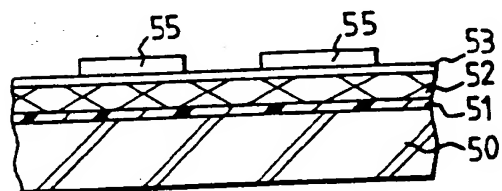


FIG. 5C

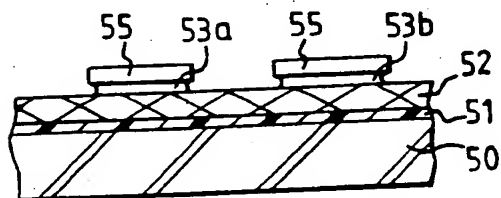


FIG. 5D

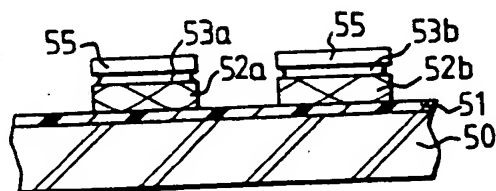


FIG. 5E

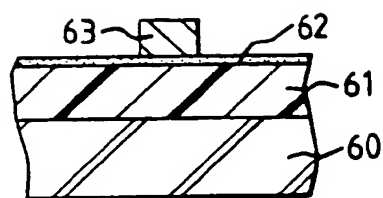


FIG. 6A

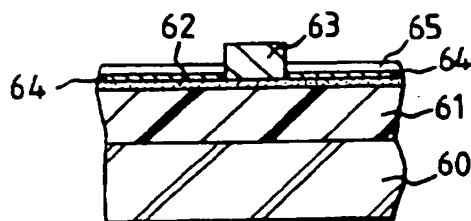


FIG. 6B

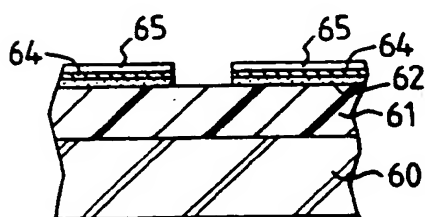


FIG. 6C

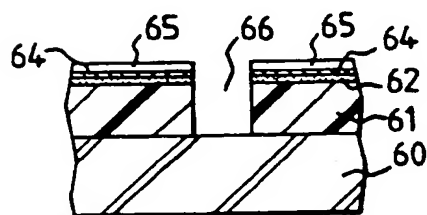


FIG. 6D

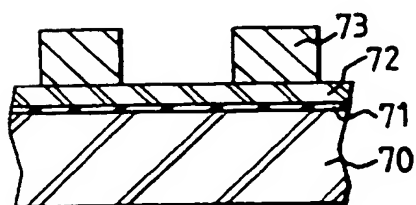


FIG. 7A

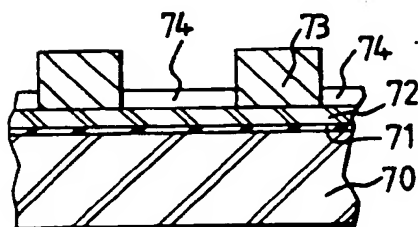


FIG. 7B

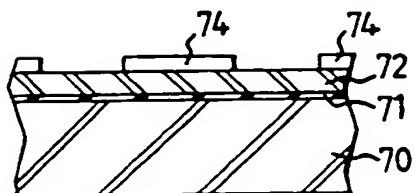


FIG. 7C

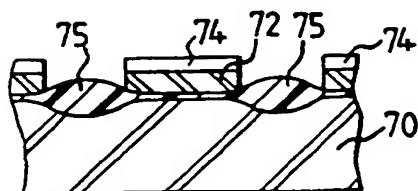


FIG. 7D

THIS PAGE BLANK (USPTO)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 630 044 A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 94114930.4

(51) Int. Cl.⁶: H01L 21/90, H01L 21/321

(22) Date of filing: 15.08.89

(30) Priority: 08.09.88 JP 223503/88

(43) Date of publication of application:
21.12.94 Bulletin 94/51

(60) Publication number of the earlier application in
accordance with Art.76 EPC: 0 358 350

(64) Designated Contracting States:
DE FR GB

(66) Date of deferred publication of the search report:
12.07.95 Bulletin 95/28

(71) Applicant: KABUSHIKI KAISHA TOSHIBA
72, Horikawa-cho
Saiwai-ku
Kawasaki-shi
Kanagawa-ken 210 (JP)

(72) Inventor: Okumura, Katsuya, c/o Intellectual
Property Div.

Toshiba Corporation,
1-1-1, Shibaura
Minato-ku,
Tokyo (JP)
Inventor: Watanabe, Tohru, c/o Intellectual
Property Div.
Toshiba Corporation,
1-1-1, Shibaura
Minato-ku,
Tokyo (JP)
Inventor: Watase, Masami, c/o Intellectual
Property Div.
Toshiba Corporation,
1-1-1, Shibaura
Minato-ku,
Tokyo (JP)

(74) Representative: Maury, Richard Philip et al
MARKS & CLERK,
57-60 Lincoln's Inn Fields
London WC2A 3LS (GB)

(54) Forming a prescribed pattern on a semiconductor device layer.

(57) A method for forming a prescribed pattern on a layer of a semiconductor device, comprising the steps of:

preparing a substrate (40) having a first main surface;

forming a first layer (41) on the first main surface;

forming a second layer (42) on the first layer;

forming a third layer (43) on the second layer;
selectively removing the third layer to form a first patterned layer;

immersing the substrate having the first patterned layer into a predetermined solution to form a fourth layer (45) selectively over the portions of the second layer uncovered by the first patterned layer;

removing the first patterned layer; and
etching the second layer using the fourth layer (45) as a mask,

characterised in that the first layer (41) is an insulating layer, the second layer (42) is a metal layer, third layer (43) is a photoresist layer, and the fourth layer is a SiO₂ layer, whereby the remainder of the second layer (42) constitutes a metal interconnect layer for the semiconductor device.

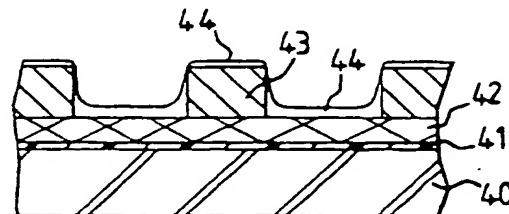


FIG. 4A

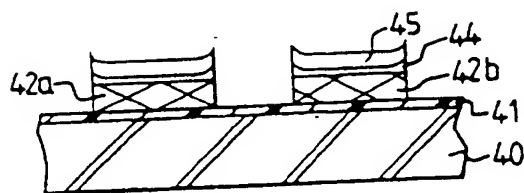


FIG. 4D



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 11 4930

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	FR-A-2 354 633 (IBM) * page 3, line 8 - page 4, line 37; figures 1-6 *	2,6	H01L21/90 H01L21/321
X,D	US-A-4 624 749 (HARRIS) * figures 1-6 *	2,6	
A,D	US-A-4 599 137 (NTT) * figure 1 *	1	
P,X	EP-A-0 304 077 (TOSHIBA) * abstract; figures *	1	
A	EP-A-0 178 619 (TOSHIBA) * abstract; figures 4,5 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			H01L
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		9 May 1995	Gori, P
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 150 (04/92) (P04001)

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)